# Sb enhancement of lateral superlattice formation in GaInP

C. M. Fetzer,[a] R. T. Lee, S. W. Jun, and G. B. Stringfellow
*University of Utah, Salt Lake City, Utah 84112*

S. M. Lee and T. Y. Seong
*Kwanju Institute of Science and Technology, Kwanju 500-712, Korea*

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Epitaxial layers of GaInP were grown by organometallic vapor phase epitaxy with small amounts of TESb added to control the surface bonding. Above a concentration of Sb/III(v)=0.016, 12 K photoluminescence measurements show that the band gap is reduced, as compared to completely disordered GaInP, by Sb addition and that polarization along the $[\bar{1}10]$ direction is as much as 41 times larger than along [110]. Transmission electron microscopy results show a lamellar domain structure in the $[\bar{1}10]$-zone axis dark-field images with a period of 120 nm. Atomic force microscopy shows surface undulations with the same period along the $[\bar{1}10]$ direction. The results demonstrate an increase in the magnitude of the presence of lateral composition modulation with increasing Sb concentration. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1350424]

A difference in lattice constants between the binary constituents of a III–V ternary alloy semiconductor results in a large, positive enthalpy of mixing which drives phase separation.[1] The growth surface of the epitaxial layer appears to determine the final microstructure. For example, in GaInP, a (2×4) reconstruction with $[\bar{1}10]$ P dimers leads to long range ordered structures.[2] In epitaxy, slow bulk diffusion kinetically prevents the epilayer from reaching equilibrium. The surface is a region of enhanced atomic motion and allows for limited phase separation, so only the phases formed near the surface during growth are observed.[3] A special form of phase separation is a spontaneous composition superlattice known as composition modulation (CM).[3–5]

Recently, the addition of small amounts of Sb during the organometallic vapor phase epitaxial (OMVPE) growth of GaInP layers has been shown to provide a degree of control of the surface. (1) It was shown to reduce $CuPt_B$ ordering by reducing the strain energy due to the surface group V dimers.[6] (2) At higher concentrations, the Sb surfactant acts to induce triple period ordering (TPO), a phase with triple the periodicity of the zincblende lattice along the [111] and $[\bar{1}\bar{1}1]$ directions.[7,8] Above Sb/III(v)=0.016 [Sb/P(v) =0.0004], Sb was demonstrated to lead to a reduction of the band gap, as measured by 20 K photoluminescence (PL).[7,8] The band-gap reduction was initially attributed to the formation of the TPO, consistent with previously published reports of the effects of TPO on optical properties.[9,10] Recent studies, presented in this letter, indicate that the band-gap reduction is not related to the TPO phase. Sb mediated growth of the GaInP layers gives samples exhibiting strong polarization of the PL due to valence band splitting, a strong indicator of the simultaneous presence of a lateral superlattice CM.[3–5] This letter describes the polarized PL of Sb enhanced OMVPE grown GaInP. The Sb modified layers show very strong polarization well exceeding that typically associated with CuPt ordering.[10–14]

The GaInP samples were grown in a horizontal flow atmospheric pressure OMVPE reactor.[15] The 0.4 $\mu$m thick epitaxial layers were grown under conditions giving nominal lattice match to semi-insulating (001) GaAs substrates.[8] The V/III ratio in the vapor was 40. This ratio allows a comparison of the Sb concentrations reported as Sb/III(v) to those for previous results reported as Sb/P(v).[6–8] This change in notation is to better indicate the amount of Sb on the surface during growth and allows a comparison of results at different growth rates. The lattice mismatch determined by x-ray diffraction was $\Delta a/a < 10^{-3}$ for the samples used in this study. A control sample was grown on (511)*A* oriented semi-insulating GaAs to produce nearly disordered GaInP without the introduction of a surfactant.[16] Triethylantimony, TESb, was used at low concentrations as a surfactant.

Polarized PL was obtained by focusing light from an $Ar^+$ ion laser operated at 488 nm to a spot diameter of 0.2 mm for a total incident power of 30 W/cm$^2$. The sample was cooled to a nominal 12 K. The luminescence was analyzed using a rotating polarizer film to select the PL polarization to be along either the $[\bar{1}10]$ or the [110] direction. The resulting PL was dispersed through a 0.5 m monochromator (SPEX 500M) and collected with a photomultiplier tube. Standard lock-in amplification techniques were used to reduce the noise and amplify the signal. All spectra were corrected for anisotropy in system response. Orthogonal ⟨110⟩ cross sections were prepared for transmission electron microscopy (TEM) and transmission electron diffraction (TED) by $Ar^+$ ion milling and examined in a JEM 2010 instrument operated at 200 kV. Atomic force microscope (AFM) images were taken using a Nanoscope IV microscope operated in tapping mode.

Figure 1 shows the results of the polarized PL for several samples. Polarized PL for the disordered GaInP grown on the (511)A substrate and undoped $CuPt_B$ samples are labeled (a) and (b), respectively. For both samples, the [110] polarization is stronger. The peak energy for the (511)A sample is 1964.3 meV. Equating the peak energy to the band gap, indicates that it is 40.7 meV lower than that of purely disor-

[a]Electronic mail: cmfetzer@xmission.com

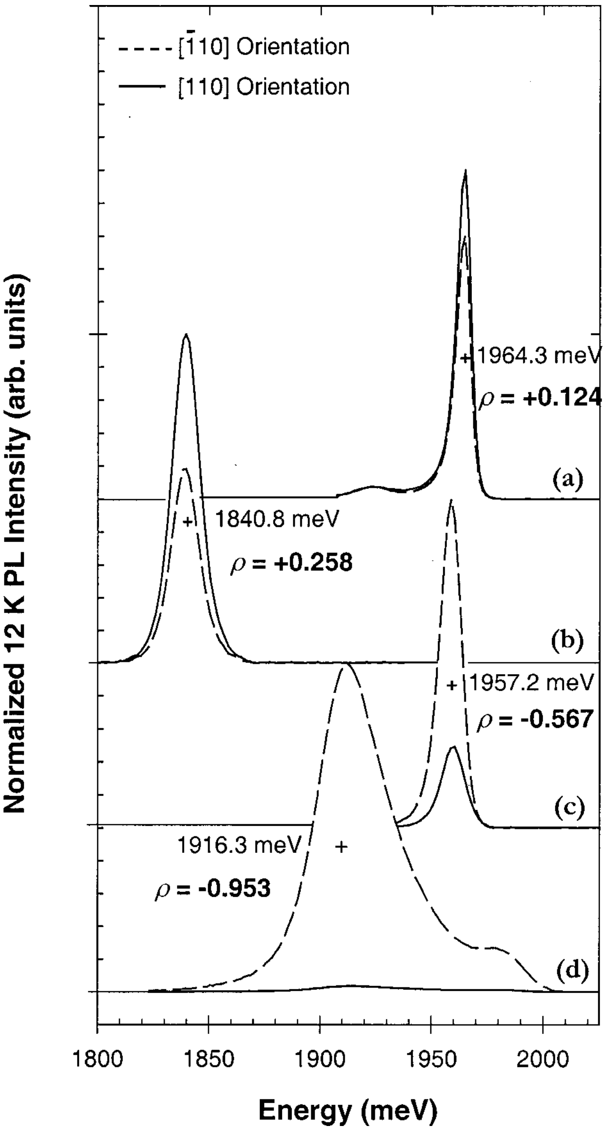


FIG. 1. 12 K polarized PL spectra for GaInP samples grown on: (511)A (a) and (001) singular (b), (c), and (d) substrates with: Sb/III(v)=0, (a) and (b); Sb/III(v)=0.016, (c); and Sb/III(v)=0.064 (d). The solid line indicates the polarizer oriented along the [110] axis and the dashed line along the [$\bar{1}$10] axis. Spectra were normalized to the most intense orientation and offset for clarity. Peak energy and polarization are also indicated next to each spectrum.

dered material, 2005 meV.[2,17] The polarization, $\rho$, is quantified as

$$\rho=\frac{I_{[110]}-I_{[\bar{1}10]}}{I_{[\bar{1}10]}+I_{[110]}}, \tag{1}$$

where $I_{[\bar{1}10]}$ and $I_{[110]}$ are the integrated PL intensities with the polarizer aligned along the two orthogonal $\langle 110\rangle$ directions. The polarization for the (511)$A$ sample is +0.124, typical of weak ordering.[17] The undoped sample, showing strong $CuPt_B$ ordering [Fig. 1(b)] has a much lower peak of 1840.8 meV and the polarization is +0.258. The band-gap reduction is 164.2 meV in this sample. These values are typical of behavior caused by $CuPt_B$ ordering.[11–14] In contrast, the addition of Sb yields a very different behavior. Spectrum (c) in Fig. 1 is from a sample grown with Sb/III(v)=0.016 and shows nearly the same band gap and full width at half maximum (FWHM) as for the (511)$A$ sample, with a peak at

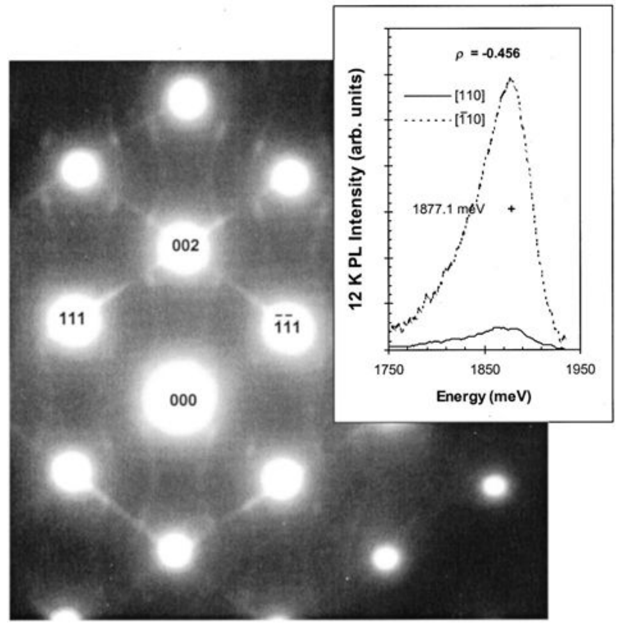


FIG. 2. TED pattern for the [$\bar{1}$10]-zone axis for sample at Sb/III(v)=0.128. The superspots at the 1/3 and 2/3 positions toward the (111) and ($\bar{1}\bar{1}$1) zincblende spots indicate triple period ordering. Polarized PL for the same sample is shown in the inset.

1957.2 meV and FWHM of 10 meV. Previous TEM studies indicate that this sample has very weak $CuPt_B$ ordering.[8,9] In contrast to the (511)$A$ sample, this sample shows a very strong polarization of −0.567. Note the change in sign relative to the $CuPt_B$ ordered samples. The [$\bar{1}$10] polarization is now 3.6 times stronger than the [110] polarization. The polarization result is remarkable since the maximum polarization predicted for single variant, perfect CuPt ordering is +0.5.[2,11–14,17] In Fig. 1(d), for Sb/III(v)=0.064, the PL peak energy has decreased to 1916.3 meV and the polarization has increased to −0.953, the largest observed in this study. The FWHM has increased to 45 meV indicating considerable inhomogeneous broadening for this sample, much larger than any undoped, $CuPt_B$ ordered sample in this study. The sample yielding the PL shown in Fig. 1(d) contains a triple period ordered (TPO) phase, with ordering occurring along the (111) and ($\bar{1}\bar{1}$1) planes determined from TEM patterns.[8,9]

It is unlikely that the PL spectra in Figs. 1(c) and 1(d) originate from TPO since the sample grown at Sb/III(v) =0.016 [Fig. 1(c)] shows no TPO and yet demonstrates a strong polarization. The inset of Fig. 2 shows the polarized PL from a sample grown at an Sb concentration double that of Fig. 1(d) [Sb/III(v)=0.128]. The spectrum shows a lower PL peak energy at 1877.1 meV and a strong polarization of −0.45. The TED pattern from Fig. 2 indicates that the TPO is weaker than that in the sample producing the PL shown in Fig. 1(d).[9] We conclude that TPO is not the cause of the unusual optical properties.

An appealing explanation of both the band-gap reduction and polarization strength is the formation of a lateral superlattice due to CM.[4,5] Single epilayers of GaInP on (001) GaAs, in particular, have already been shown to produce lateral CM with the modulation along the [110] direction.[18] Lateral CM is known to result in a reduced band gap as

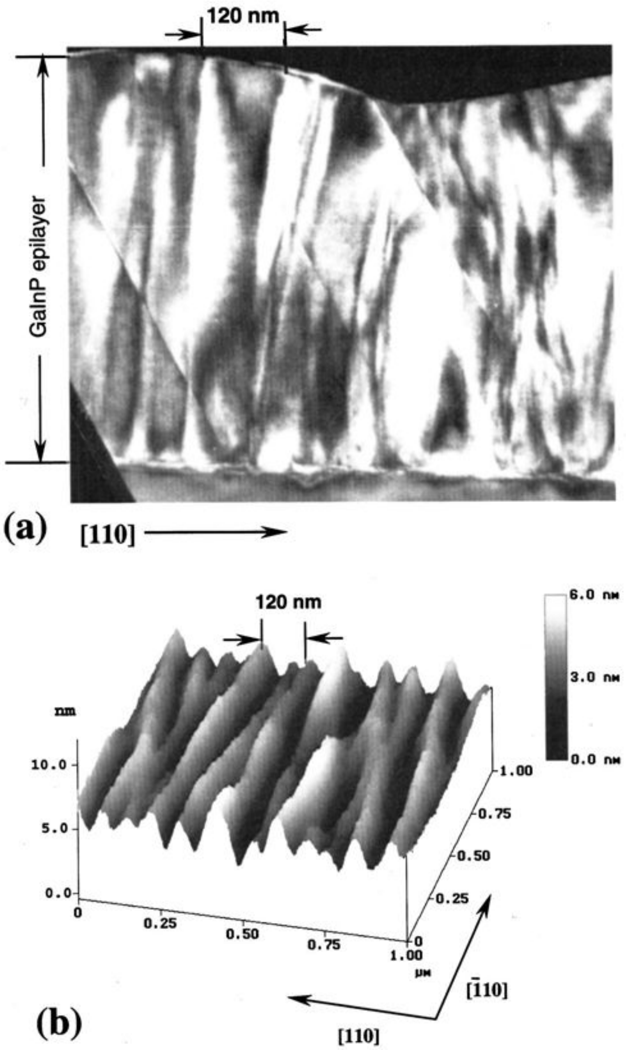


FIG. 3. (a) Dark-field TEM image of the cross section in the [$\bar{1}$10]-zone axis. (a) Bright and dark regions correspond to compressive and tensile strained regions and hence different compositions. The period of the modulation along [110] is 120 nm. (b) 1 $\mu$m$\times$1 $\mu$m AFM image of the surface. The surface shows undulation along the [110] direction with a period of 120 nm and an average height of 6 nm. The elongated ridges along the [$\bar{1}$10] direction are ~2–5 $\mu$m in length.

observed by PL, an increase the FWHM of the PL, and a very strong polarization.[4–6,18]

Strained lamellae lateral to the growth direction are observed by TEM in the [$\bar{1}$10]-zone axis dark-field image of the sample grown at Sb/III(v)=0.064 in Fig. 3(a). The image, taken from the (002) zincblende spot, shows clear alternating light and dark domains extending from the GaAs substrate to the sample surface. The period of the domains is ~120 nm. The domains are seen only in the [$\bar{1}$10] image and are missing from the [110] image, indicating a lamellar structure is formed lateral to the growth direction. This structure is typical of the CM observed in other alloy systems.[4–6,18] The period observed here is almost an order of magnitude larger than CM in GaInP produced by gas source molecular beam epitaxy.[18]

Further confirmation of the CM is given by AFM. The AFM image of the sample shown in Fig. 3(a) is shown in Fig. 3(b). The surface shows a very regular surface undulation with an average height of 6 nm and a period of 120 nm, elongated along [$\bar{1}$10] and modulated along the [110] direction. Such surface undulations are typical of the formation of lateral CM, both in direction and regularity.[3,4] The undulations form to reduce the system free energy by partially relieving the strain energy due to phase separation. Similar undulations with the same period, but a smaller amplitude are observed for Sb/III(v)=0.016. As the amount of Sb in the vapor is increased, the PL peak energy decreases and surface undulation height increased. The results indicate an increase in CM amplitude with increasing Sb.

The addition of Sb during the OMVPE growth of GaInP is shown to produce lateral CM. Polarized PL, TEM, and AFM indicate that lateral CM increases with increased Sb on the surface. Spectra from polarized PL show that the polarization increases to $-0.953$ as the band gap reduced to 1916 meV. TEM dark field images indicate lamellar domains of CM modulated along the [110] direction with a period of about 120 nm are present. AFM results show surface undulations with the same period and increasing in height with increasing Sb concentration.

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